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Fig.1.

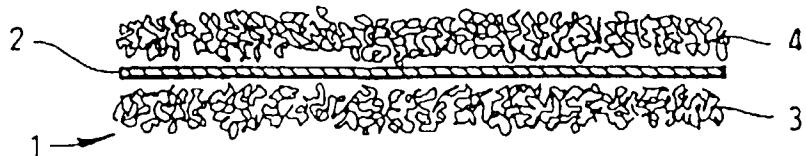


Fig.2.

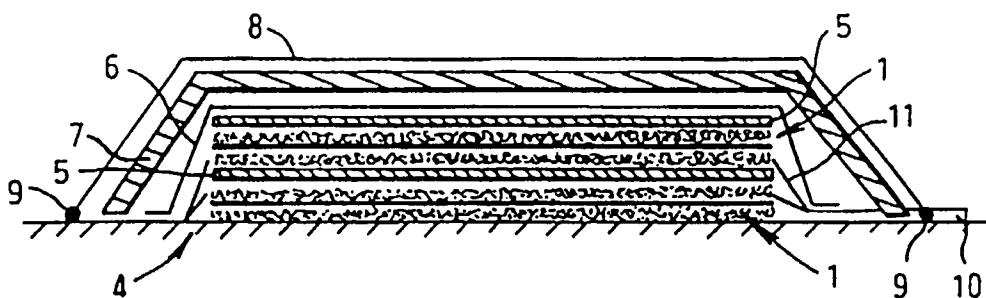
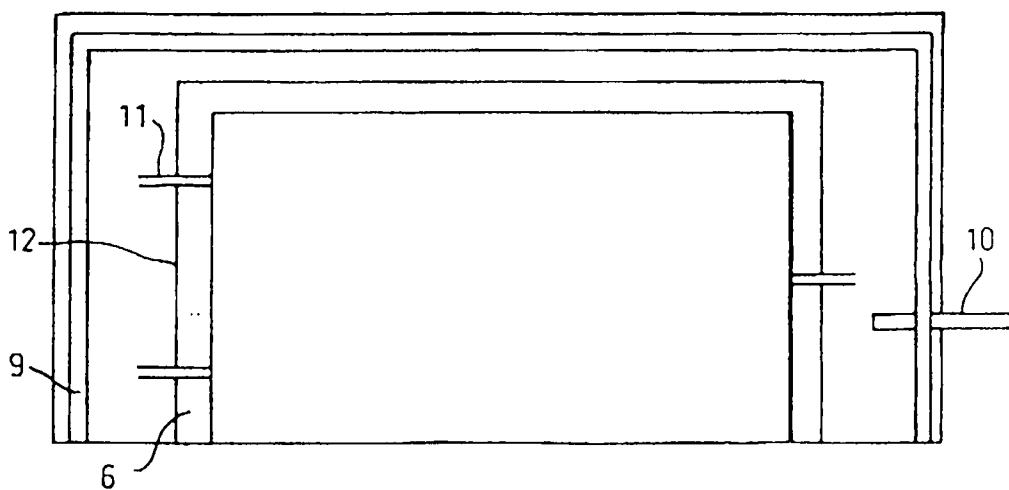


Fig.3.



MOULDING MATERIALS

The present invention relates to moulding materials. More particularly, it relates to composite moulding materials 5 which include fibres in their structure which in the moulded product will provide reinforcement.

Historically, mouldings were formed from resin either alone or reinforced with fibres. However, whilst in principle the 10 products were satisfactory, where fibres were present, it was difficult to control the ratio of the resin to the reinforcement fibres and thus the quality of the products produced was not consistent. The process was therefore refined such that the supplier of the resin provided the 15 producer of the moulded article with a pre-impregnated reinforcement known as a "prepreg". The moulder is then able to produce the moulded article from the pre-impregnated material confident that the ratio of resin to fibre is correct. Thus, the present invention is 20 particularly directed to preformed prepgs.

It will be understood that conventionally "prepgs" are fibrous composite materials which comprise fibres embedded in a matrix of resin and which are provided in the form of, 25 for example, sheets, strips, or continuous rolls, which can then be placed in contact with a mould prior to the resin being cured to form the moulded product. A prepg may comprise unidirectional fibres or the fibres may be multi-directional. In use, several layers of prepg may be 30 layered prior to curing to form a laminate product.

The most basic form of prepg is prepg tape or strip. These tapes or strips comprise unidirectional non-woven fibres held together by resin. These tapes are attractive 35 as the straight fibres provide the finished moulding with

good mechanical properties. Further the good packing of the fibres reduces the amount of resin required in the laminate. However, as these tapes have little porosity through their thickness, when multiple layers are used 5 together the tapes or strips trap substantial volumes of air which will lead to voids in the cured laminate.

For the purposes of this application the term prepreg will be used to refer not only to composite materials where the fibres are embedded in the resin but also to those where 10 they are in contact with it.

Howsoever formed, when such prepgs are layered to produce a thick laminated product, certain drawbacks and disadvantages can arise. A thick laminated product is 15 generally understood to have a thickness greater than 2mm and is preferably greater than 4mm and may extend to 40mm.

A particular disadvantage of such thick products is that air can become trapped either within a layer of the 20 moulding material or between adjacent layers. The presence of intra-, inter- or intra- and inter-laminar air can lead to voids being formed in the finished cured product. Such voids can result in the laminate having reduced mechanical properties and can lead to premature failure of the 25 composite material.

Many techniques have been suggested to reduce the occurrence of such voids. One such technique is that of frequent vacuum debulking in which a few layers are laid in 30 the mould and consolidated using vacuum before further layers of moulding material are laid onto the laminate formed in the first step. However, whilst this technique may go some way to addressing the problem of void formation, a void content of 2 to 5% will still commonly be 35 present. Further, the technique of vacuum debulking, whilst

being somewhat effective, is labour intensive and is therefore costly and hence not desirable.

The problem of void formation is particularly exacerbated
5 when heavyweight material, for example 1200 g/m² glass
fibre unidirectional tape, is used in the production of the
moulding. It will be understood that it is desirable to use
heavyweight materials in moulding production since their
use makes it possible to produce the finished product from
10 fewer layers thereby reducing the costs both of labour and
materials. However, where heavyweight material of this kind
is used, void formation is particularly prevalent since
such materials are generally impervious to air movement
through their thickness.

15 It has been suggested that interleaving dry reinforcement
layers between the layers of the prepreg as the laminate is
built up can reduce the problem of void formation. However,
whilst this technique does go some way towards addressing
20 the problem of void formation, the presence of the dry
reinforcement layer reduces the relative resin content of
the finished product which may have a detrimental effect on
the strength of the finished product. Whilst it is possible
25 to compensate for the loss of resin from the prepreg to the
dry reinforcement layers by providing additional resin in
the prepreg, such increased resin content materials are
difficult to handle because of their high tack and low
drape. It is also important that there is complete
30 coincidence of the resin rich prepreg and dry layers
throughout the laminate or resin rich or resin lean areas
will result.

A similar assembly to the above described interleaved
laminate is disclosed in document US-A-4 311 661. This
35 document describes a process for producing a resin-fibre

composite article with a relatively low void content. The process comprises the step of forming an assembly on the surface of a mould, the assembly comprising individual layers consisting of a resin film, fibrous reinforcement 5 layers, a porous parting film and a bleeder layer which are each individually laid up. The process further comprises the step of applying a vacuum to the assembly and heating the assembly to cause the resin film to melt and impregnate upwards from the mould surface through the reinforcement 10 layer, the porous parting film and into the bleeder layer to completely saturate both the fibrous reinforcement layer and the bleeder layer. After the impregnation stage, the assembly is further heated at a sufficient temperature and pressure to effect final curing of the resin. After curing, 15 the composite article is retrieved by removing the bleeder layer and the parting film from the assembly.

A disadvantage of this particular process is that the resin layer, reinforcement layer and bleeder layer are each laid 20 up separately which is labourious. Also, the process is unnecessarily complicated because of the requirements of a bleeder layer and a parting film which need to be installed and later removed. To achieve a complete wetting out of both the reinforcement layer and the bleeder layer by 25 upward impregnation, the evacuation time and vacuum pressure depend on the thickness of the reinforcement layers in the assembly. For a large thickness of reinforcement material, the evacuation time can be substantial. Another problem associated with this material 30 is that it requires handling of a resin film. These films are either hard, brittle, inflexible materials which do not adapt to the shape of the mould when they are laid up, or these films are soft, tacky and sticky which prevents them from being easily handled and re-positioned in the mould. 35 The form of the film during handling depends on its

formulation and temperature. A further problem is that it is difficult to achieve an optimal ratio of the reinforcement material and the resin material. For a particular assembly, the required optimal amount of resin 5 must be found by trial and error. Another problem is that of tailoring of the assembly. In most composite structures the laminate is not uniform. The laminate is normally made thinner in areas of low loads or stresses and reinforced (thicker) in areas of high loads or stresses. This process 10 is called tailoring. In the process of document US-A-4 311 661, tailoring requires adaptation of both the resin film and the reinforcement layers which is labour intensive. If any tailoring has not been achieved correctly (the resin/reinforcement fibre ratio is not optimal in the 15 laminate locally) the structure of the moulded article is impaired.

Document DE-A-35 36 272 relates to a method of fabricating a composite part from a pre-shaped moulding material in a 20 mould. According to this method, the preshaped moulding material comprises a layer of a resin material and a layer of a fibrous material. The resin layer is formed in the shape of the mould (pre-shaped) before it is laid up. This is achieved by forming a support film (foil) in the shape of 25 the mould and spraying resin material onto the film. After the resin layer is shaped, dry fibrous material is provided on the resin layer. The pre-shaped moulding material is processed in the mould by applying both pressure (vacuum) and heat.

30 Similar to document US-A-4 311 661, the evacuation time depends on the thickness of the fibrous layers, and consequently, for thick layers of reinforcement material, the evacuation time can be substantial to achieve complete 35 impregnation of the fibrous layers. Other disadvantages of

this method are that during the composition of the moulding material outside the mould, a support film is necessary to support the material. Fabrication according to this method is therefore complicated and inefficient, since it requires 5 an additional pre-shaping step of the material before the material is laid up in the mould. Finally, for a particular composite part, the optimal reinforcement/resin ratio along every position of the mould surface must be established by trial and error, since the thickness of both the resin 10 layer and the reinforcement layer may vary depending on the shape of the mould.

Both of the afore described methods are impractical and difficult to use in a production environment, particularly 15 in a production environment in which complex moulds and moulds of varying shapes are used. The afore described methods are also complicated and require a lot of expertise and skill from the fabricator.

20 We have now found that the aforementioned problems can be solved by the provision of a multi-layered moulding material comprising a layer of resin material and conjoined to at least one surface thereof a fibrous layer.

25 Thus, according to a first aspect of the present invention, there is provided a preform multilayered moulding material according to any of the accompanying claims.

In an embodiment of the invention, the fibrous layer may be 30 held in place by the inherent tack of the surface of the resin layer. In a further embodiment, the fibrous layer may be partially impregnated by resin.

In an embodiment of the invention, the resin layer may 35 itself be a conventional prepreg.

In a particularly preferred embodiment, the multi-layered moulding material comprises three layers wherein a central resin layer has a fibrous layer conjoined to either side.

- 5 In one alternative arrangement, the multi-layered moulding material comprises five layers in which the two outer layers are dry fibrous layers each attached on its inner surface to a resin film layer. The resin film layers are themselves adhered to a further dry fibrous layer which
- 10 forms the central (fifth) layer. The resin layers in this multilayered material may be formed from different resins.

Larger multi-layered structures may also be formed in which dry fibrous layers are attached to a resin film layer.

- 15 Again, the resin film layers in this multi-layered material may be formed from different resins.

The resin layer may be a conventional prepreg.

- 20 Thus, in one particularly preferred embodiment, the outer surface of the moulding material is free from resin and is therefore dry to the touch due to the presence of the two fibrous layers and can therefore be handled readily.

- 25 In one alternative arrangement, the multi-layered moulding material may have a tackifier or a binder material applied to at least one surface.

- 30 Without wishing to be bound by any theory, it is believed that when the material of the present invention is used alone, laminated with further layers of moulding material of the present invention or laminated with layers of conventional prepreg, the fibrous layer of the material of the present invention performs in a similar manner to the
- 35 dry layers of reinforcement of the conventional systems, in

that it allows entrapped air to pass out of the laminate.

The void content for a product produced from, or including,
the moulding material of the present invention will
5 generally be less than 2% and is commonly less than 0.5%.

One particular benefit of the arrangement of the present
invention is that the amount of resin present in the multi-
layered moulding material can be controlled such that when
10 the material is cured, the correct amount of resin will
flow into the dry fibrous layers and there will be no
reduction in the cured resin content.

The moulding material of the present invention surprisingly
15 offers a number of advantages over the conventional
moulding materials. One particular benefit of the present
invention is that the moulding material exhibits improved
handling characteristics when compared to those of
conventional materials in that it is more flexible, that is
20 to say it has improved drape and can therefore be used in
the production of more complex mouldings. It has been found
that the moulding material of the present invention having
a fibre weight of 3,500 g/m² has better drape than a
25 comparable conventional prepreg having a fibre weight of
1,700 g/m².

Further, it has been found that the moulding material of
the present invention exhibits significantly lower tendency
to bridge across details in a moulding. Without wishing to
30 be bound by any theory, we believe that this is due to the
abilities of the plies to slide over each other during the
consolidation and curing stages. Further, even if bridging
does occur, the moulding material of the present invention
tends to fill any bridged areas with resin rather than
35 leave a void in the laminate. Again, without wishing to be

bound by any theory, we believe that this is due to the fact that the potential void has been evacuated by the excellent air transport properties of the material of the invention and thus resin can fill the potential void as no 5 air is trapped. By this means a high quality finished product may be obtained. This is in contrast to conventional materials, where imperfections may be noted in the surface of the moulding at complex mould areas, such as corners due to bridging of mould areas by the moulding 10 material. It is therefore possible to use the moulding material of the present invention in the production of more complex shapes than has been achievable heretofore.

In conventional prepgs that are processed under vacuum 15 consolidation, it is important that dry areas of reinforcement fibres are avoided since they generally do not completely wet out during the production of the prepg which may lead to areas of weakness in the finished product. However, where the moulding materials of the 20 present invention are used, the fibrous layer is specifically not wet out during production of the prepg but will be completely wet out during the processing.

As the improved moulding material of the present invention 25 exhibits these improved characteristics, it is possible to use heavier weight prepgs than has been possible using conventional prepg technology. With conventional technology, even when heavy weights are produced, they are difficult to handle and therefore are not desirable. 30 However, since the moulding materials of the present invention exhibit improved drape characteristics, even heavier weight prepgs may be handled readily.

Any suitable thermoset resin may be used in the production 35 of the moulding material of the present invention.

Particularly suitable resin systems include the epoxy, polyester, vinylester, polyimide, cyanate ester, phenolic and bismaleimide systems. Suitable epoxy resins include diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, epoxy novolac resins and N-glycidyl ethers, glycidyl esters, aliphatic and cycloaliphatic glycidyl ethers, glycidyl ethers of aminophenols, glycidyl ethers of any substituted phenols, monomers containing methacrylate groups (such as glycidyl methacrylates, epoxy acrylates and hydroxyacrylates) and blends thereof. Also included are modified blends of the aforementioned thermosetting polymers. These polymers are typically modified by rubber or thermoplastic addition.

Any suitable catalyst may be used. The catalyst will be selected to correspond to the resin used. One suitable catalyst for use with an epoxy resin is a dicyandiamide curing agent. The catalyst may be accelerated. Where a dicyandiamide catalyst is used, a substituted urea may be used as an accelerator. Suitable accelerators include Diuron, Monuron, Fenuron, Chlortoluron, bis-urea of toluenediisocyanate and other substituted homologues. The epoxy curing agent may be selected from Dapsone (DDS), Diamino-diphenyl methane (DDM), BF₃-amine complex, substituted imidazoles, accelerated anhydrides, metaphenylene diamine, diamino diphenylether, aromatic polyetheramines, aliphatic amine adducts, aliphatic amine salts, aromatic amine adducts and aromatic amine salts. Also suitable for systems containing acrylate functionality are UV photoinitiators such as those which liberate a Lewis or Bronstead acid upon irradiation. Examples include triarylsulphonium salts which possess anions such as tetrafluoroborate or hexafluoroborate.

The resin system may also include additives relevant to the

production of the moulding such as hardeners. Other additives may be included to effect the finished moulding such as pigments, UV stabilising additives, anti-mould, anti-fungal and flame retardant additives. Whatever 5 additives are added, it is important to ensure that the viscosity of the resin is sufficiently low during the curing and consolidation steps. If it is not, it will not wet out the dry layers.

10 The fibre layer or layers may be formed from any suitable fibres. Suitable fibres include glass fibres, carbon fibres and polymeric fibres such as polyethylene fibres and aramid fibres. Suitable glass fibres include those made from E-glass, S-glass, C-glass, T-glass or R-glass. Suitable 15 aramid fibres include those sold under the trade marks KEVLAR and TWARON HM. Ballistic grade aramid fibres may be utilised where this characteristic is required due to the intended use of the finished product. Organic fibres and modified organic fibres such as jute or hemp may also be 20 used.

25 The fibrous layer may comprise fibres of only one kind or different types of fibre may be combined in the fibrous layer.

30 The fibres may be used alone or in combination. The fibres may be used in the form of tissue, chopped strand mat, continuous mat, woven fabrics, stitched fabrics, or simple rovings. Any suitable fibre size may be used. Particularly 35 preferred are E-glass yarns having a filament diameter of 5 to 13 μ m and 11 to 136 tex or E-glass rovings having a filament diameter of 10 to 16 μ m and 600 to 2400 tex. The fibrous material may be preformed before being laid on to the resin layer or alternatively, loose fibres may simply be laid onto the resin layer.

In a particularly preferred arrangement, the fibres are arranged such that they are unidirectional. Where the moulding material of the present invention comprises two fibrous layers conjoined to opposing faces of the resin 5 layer, the fibrous layers may be orientated in the same direction or in different directions. In particular, the fibre orientation of the skins of the sandwich material may be 0°, 90°, 0°/90°, +/-45° or quasi isotropic or 0°/+45°/-45°.

10

In an embodiment of the invention the adhesive properties of the resin layer may be sufficient to retain the fibrous layer howsoever formed in position. In another embodiment the fibrous layer may be retained against the resin layer 15 by means of an adhesive. It will be understood that the adhesive will not prevent the travel of the resin into the fibrous layer during production of the product.

20

In one alternative embodiment, a tackifier and/or a binder material may be applied to one or both surfaces of the multi-layered moulding material. The tackifier/binder is preferably applied as a light covering. Typically, the tackifier/binder may be applied in an amount of 0.5% to 7% of the fibre weight.

25

The presence of the tackifier/binder serves a number of functions. First, it may provide a degree of tack to the surfaces of the material therefore assisting adjacent layers of material to be held together during processing.

30

Secondly, the presence of the tackifier/binder serves to stabilise the fibrous layers and thereby improves the integrity of the surface of the prepreg. This is particularly important where the fibrous layers on the 35 faces of the improved prepreg are made from pure rovings or

tows of fibres rather than of woven or stitched materials. The material of this embodiment may have improved handling characteristics and may be less likely to be damaged by handling prior to moulding.

5

Where a tackifier/binder is present, it may also serve as an interply toughening agent which can give significant improvements in interply fracture energy.

10 Any suitable material may be used as a binder/ tackifier. Particularly suitable materials include high molecular weight resins. These resins may be used alone or in combination with additives including toughening agents and curing agents.

15

The tackifier/binder may be applied to the material by any suitable means including spraying using carrier solvent, hot melt techniques or dry powder applications. In a particularly preferred arrangement, the tackifier/binder forms discrete particles on the surface of the fibres rather than a uniform coating. The tackifier/binder may be applied to the material at any suitable time during its manufacture.

25 The arrangement of the structure of the fibres in the fibrous layer or of the fibrous layer itself may be altered depending on the properties required to be exhibited in the finished end product. For example, where the product is to be a high performance composite mould tool, it is preferable to use discrete areas of reinforcement rather than continuous lengths. Conventionally, these small areas are of the approximate size 300mm x 300mm. Although the use of fibrous materials having discrete areas of reinforcement offer a range of benefits, they have not generally been accepted by some fabricators in the past as their use is

labour intensive. This is particularly the case where the moulding is large in size and comprises several layers. In this connection, it is noted that in the fabrication of, for example, composite tools, the moulding may be made of 5 about 20 layers and be 20 to 50 m² in area.

It will be understood that a moulding material in accordance with the present invention may be readily formed by laying pieces of fibrous material, of the desired size 10 onto the resin layer. Thus according to a further preferred aspect of the present invention there is provided a moulding material in which the or each fibrous layer comprises discrete pieces of fibrous material. Thus the fibrous layer may be discontinuous.

15 The benefit associated with materials formed in this way is that the fabricator can simply roll out the material and the need to separately attach, for example, squares of fibrous material is obviated. As with conventional 20 materials, the materials with these discrete areas of fibres nest down to conform to the tool profile and the risk of bridging areas of the mould leading to the formation of voids is further minimised. The reduced fibre 25 length present in a material of this type also reduces stresses which may arise in the finished laminate. These stresses result from thermal or cure shrinkage and may result in delamination or even change of shape of the tool.

30 The discrete panels of fibrous material used to form the fibrous layer of the moulding material of the present invention are preferably squares 300mm x 300mm. Where the moulding material comprises two fibrous layers located on opposing faces of the resin layer, the discrete panels are 35 preferably arranged such that the joints between panels on the upper layer are staggered from those between panels in

the lower layer. Thus the inherent strength of the material is not compromised.

5 The moulding materials of the present invention may be formed readily by contacting the resin layer with the or each fibrous layer.

10 Thus, according to a second aspect of the present invention there is provided a method of forming a moulding material in accordance with the above first aspect of the invention 15 in which a fibrous layer is placed in contact with a resin layer.

15 The moulding material of the present invention may be made by any suitable method. However, hot-melt techniques are particularly preferred.

20 In one method, the resin mixed with catalyst and any additives is preferably coated onto a support, such as siliconised paper substrate prior to being contacted by the fibrous layer. The resin is preferably coated onto the substrate using a conventional filmer. The coating is 25 preferably laid onto the substrate at a raised temperature. The temperature selected will depend on the resin used, however a suitable temperature will be in the region of 60°C.

30 The weight of the resin coated on the support will depend on the properties required of the finished prepreg. However, the weight is generally from 20 to 1,200 g/m² .

The coated substrate may be passed over a chill plate at about 5°C to reduce the temperature of the resin.

35 Where it is desirable to form a moulding material having

fibrous layers located on both sides of the resin layer several methods are available. In one method, two prepgs are formed as described above, the substrates are removed and the two prepgs are then combined with the two 5 resinous sides being placed together such that the fibrous sides are located apart from each other such that they are on the outer faces of the resulting sandwich. When the two resin layers unify the resulting moulding material has a central resin layer conjoined on each face to a fibrous 10 layer.

In one alternative arrangement, a moulding material comprising a resin layer and a single fibrous layer produced as described above is turned such that it lies on 15 the dry fibrous layer, the support is removed and a fibrous layer may then be placed on the exposed resin surface.

In another method a carrier fabric or tissue is coated on both sides with a resin film and the dry fibrous layers are 20 combined onto each face of the resin film.

In a further alternative method, a fibrous layer is laid as a support and the resin layer is then coated thereon. The second fibrous layer may then be readily laid onto the 25 exposed surface.

The process may be mechanised and may be a batch process or a continuous process.

30 Once the moulding material of the present invention is formed it may be rolled. An interleave material may be used. A particularly suitable interleave material is a polyethylene interleave.

35 The moulding material of the present invention may be

readily stored until required. The shelf life will be dependant on the resin system. It is preferable that the material is stored at temperatures below zero (most preferably -18°C to -4°C). At ambient temperature, the 5 product has a shelf life in the region of 5 to 55 days, dependant on resin system and fibre weight. After the expiry of the shelf life period, the product is still usable but will have the characteristics and properties of conventional prepgs.

10

Moulding materials of the present invention or made in accordance with the second aspect of the present invention may be used alone, laminated with further layers of moulding material of the present invention or laminated 15 with conventional prepg materials. The materials may be processed by any suitable method and are preferably cured by means of a vacuum processing technique to form high quality laminates.

20

A further advantage of the moulding material of the present invention is that the thick section, i.e. one having thickness greater than 4mm, preferably about 10mm, may be produced in a single operation with no requirement for intermediate consolidation debulking stages.

25

Where a vertical mould surface is to be coated, a combination of the moulding material of the present invention is preferably used in combination with conventional prepgs as the high tack of the conventional 30 material will help to hold the material of the present invention in place. Alternatively, a moulding material of the present invention coated with tackifier/binder may be used.

35 The moulding material of the present invention is

particularly suitable for use in combination with prepreg tape. The combination of the moulding material of the present invention and the prepreg tape is particularly advantageous since the material of the present invention 5 allows the tape to breathe such that void formation is reduced or even obviated. Further, the arrangement allows even poor quality tapes having dry or partially wet out fibres to be used since on curing the fibres will wet out completely such that a high quality laminate is formed.

10

In use, once the layers of the laminate have been laid into the mould, the resin is cured. It is desirable that a cure schedule is selected whereby the temperature is held at a point where the resin viscosity is low. The cure schedule 15 selected will depend on the resin used.

Particularly improved results in processing the material of the present invention may be obtained where care is taken to ensure that the dry fibrous layers are in contact with a vacuum system to ensure that entrained air can be fully 20 evacuated. One method of achieving the contact between the dry fibrous layers and the vacuum system is to cut the moulding material of the present invention larger than is conventional and then linking it to the vacuum system via an air breathable media. Suitable media include a non-woven 25 breather, woven breather or dry fibrous strands or tows. Suitable non-woven breathers include nylon felted material of 150 g/m².

Where required a coating may be applied to the moulding.

30 The coating may comprise a conventional gel coat system. Suitable gel coat systems include epoxy with the incorporation of a variety of fillers and pigments. Polyester or vinylester gelcoats may also be used.

35 Whilst these gel coats, provide satisfactory results, they

are labour intensive to use. We have now found that an improved coating may be obtained by the use of a modified moulding material of the present invention which is used as the layer closest to the mould. The modified moulding 5 material comprises a layer of resin having a lightweight woven cloth on one face and a non-woven tissue on the other face. This material applied to a tool with the woven cloth facing the mould and backed up with either a conventional moulding material or a moulding material in accordance with 10 the present invention gives a high quality surface substantially free of pinholes or surface porosity.

Thus according to a further aspect of the present invention there is provided a moulding material for use in the 15 production of a surface layer comprising a resin layer having a fibrous layer conjoined to each surface thereof. The material conjoined to one surface is preferably a woven material and the layer conjoined to the opposing surface is preferably nonwoven. The fibrous layers are preferably 20 produced from glass fibres. A light weight fibrous layer, typically 20gm/m².

The woven surface layer generally wets out during the consolidation process. Any suitable woven cloth may be 25 used. However, in a particularly preferred arrangement the material is selected to have a good light stability and to improve the appearance of the finished product.

The moulding materials of the present invention may be used 30 in the production of a wide range of products. Examples include products used in the marine industry such as boat hulls, masts, spars; the aerospace industry such as fuselage parts; the motor industry such as car, van or lorry body parts; the sports industry such as surf boards, 35 sailboards, and other sports equipment such as bicycles or

hockey sticks, and those used in other industries such as composite tools, composite tubes and turbine blades such as those used in wind turbines.

5 Thus, according to a further aspect of the present invention there is provided an article of manufacture produced from the moulding material of the first aspect of the present invention or made in accordance with the second aspect of the present invention. There is also provided a
10 method of forming the article of manufacture in which the moulding material is placed in contact with a mould and then allowed to cure.

15 The moulding material of the present invention may be used alone or laminated with one or more layers of moulding material in accordance with the present invention or conventional moulding materials.

20 The invention will now be described by way of example with reference to the accompanying example drawings in which:

Figure 1 is schematic diagram of a three layered moulding material in accordance with the present invention;

25 Figure 2 is schematic diagram of the apparatus used in the production of the moulding material of the present invention; and

30 Figure 3 is schematic diagram of an alternative apparatus.

As illustrated in Figure 1, the moulding material of the present invention 1, comprises a central resin film 2 having fibrous layers 3 and 4 located on opposing faces

thereof.

In use, this material 1 is laid on the tool surface 4. The material may be laminated with other materials of the 5 present invention or with conventional prepgs. In the arrangement illustrated in Figure 2, two layers of moulding material in accordance with the present invention is interleaved with layers of conventional prepg 5. This stack is preferably surrounded by a non-perforated film 6, 10 a breather 7 and a vacuum film 8. The vacuum film 8 is sealed to the tooling by means of sealant tape and the air is evacuated during the curing process via vacuum line 10.

Curing is preferably effected at temperatures above 15 ambient.

Glass rovings 11 may be utilised to assist the perimeter air bleed. These glass rovings are particularly advantageous where a zero bleed mode of processing is used. 20 The glass rovings are put through the non-perforated film to assist in the evacuation of air from the laminate stack. To further assist the removal of air, glass rovings may be placed through the non-perforated film in the centre of the panel. These allow air to bleed from the centre of the 25 panel and also connects the moulding materials of the present invention in the laminate together in the z-axis thereby further assisting evacuation of air.

When making sandwich laminates in one operation it is 30 beneficial to have air bleed holes in the core. These allow the air to escape from the underlying laminate thus preventing any closing off of the material under the foam block. Saw cuts in the lower face of the core around the perimeter may also be used to eliminate any closing off 35 effects of the core edge. The saw cuts are typically 2mm

deep by 1 mm wide and end 8cm long at a spacing of every 8cm.

5 The apparatus illustrated in Figure 3 is very similar to that of Figure 2 but is appropriate for use with a large laminate stack.

10 A suitable cure schedule involves holding the temperature at a point where the resin viscosity is low, for example, 10 poise to 100 poise for a period of 4 hours, and remains low for sufficient time for the resin to wet out the fibres of the fibrous layer or layers. A typical cure schedule would be to ramp from 25 to 70°C, a dwell at 70°C for four hours, ramp to 85°C and then held at 85°C for 10 hours. On 15 this schedule a typical resin viscosity would drop down to 40 poise and at the end of the four hour dwell has only risen to 100 poise. The ramp rates to 70°C or 85°C are not critical. However, they will normally be in the range of 0.1 to 10°C/min.

20

Example 1

25 A prepreg according to the present invention was formed by laying unidirectional E-glass woven reinforcement of 500 g/m² on opposing sides of a layer of 430 g/m² resin. This prepreg was interleaved with layers of conventional prepreg tape of 1200 E-glass with a resin content of 30% by weight. In both types of prepreg the resin used was the SP Systems 30 SE90 available from SP Systems of Structural Polymer (Holdings) Limited of Isle of Wight. The resin is a high flow, 85 to 120°C cure, non-toughened epoxy prepreg cured by an accelerated dicyandiamide curing agent. SE90 prepreg is an epoxy prepreg.

35 The laminate stack was then covered with nylon peel ply and

a microperforated release film, a layer of 150g non-woven breather material and an impervious nylon vacuum bag.

A vacuum of 90% was applied and the assembly heated from
5 ambient to 70°C at 0.3°C/min. The temperature was then held at 70°C for 4 hours. The temperature was then ramped up to 120°C and then held for one hour. The laminate was then cooled to ambient temperature and the laminate was demoulded and examined.

10

On examination it was noted that the dry reinforcement layers had completely wet out and the laminate was free of entrapped air.

15

The void content of the laminate was determined by measuring the specific gravity of the sample by weighing it in air and water. The laminate was then put in an oven at 650°C to burn off the resin. From the weight loss and the densities of the resin and the glass, the void content was
20 calculated. Measurements showed the void content to be less than 0.25%. The final fibre volume fraction was 56%.

25

Whilst the moulding material of the present invention has been described as having at two or three layers, it will be understood that a multi-layer moulding material in accordance with the present invention, may be supplied to the fabricator in an arrangement which comprises more than three layers due to the combination of several layers of the moulding material of the present invention together.

30

CLAIMS

1. A preform multi-layered moulding material adapted for use in multiple layers, said multi-layered 5 moulding material comprising a layer of resin material and having conjoined to at least one surface thereof a fibrous layer by contacting the respective layers without any substantial impregnation, said fibrous layer of said moulding material being held to said resin layer by 10 inherent tack of the adjacent surface of the resin layer such that said fibrous layer is at least partially unimpregnated with said resin to allow entrapped air to pass out of said multi-layered moulding material during processing of the material.

15

2. A multi-layered moulding material according to claim 1 wherein a first fibrous layer is conjoined to the upper surface of the resin layer and a second fibrous layer is conjoined to the lower surface of the resin layer.

20

3. A multi-layered moulding material according to claim 2, wherein the outer surface of the moulding material is free from resin and is dry to touch.

25

4. A multi-layered moulding material according to claim 2 or 3 wherein the first and second fibrous layers are formed from the same material.

30

5. A multi-layered moulding material according to claim 2 or 3 wherein the first and second fibrous layers are formed from different materials.

35

6. A multi-layered moulding material according to any one of claims 1 to 5 wherein the or each fibrous layer before contacting is partially impregnated by resin.

7. A multi-layer moulding material according to any

one of claims 1 to 6 wherein a tackifier and/or a binder is applied to one or both outer surfaces of the at least one fibrous layer.

5 8. A multi-layer moulding material according to any one of claims 1 to 7 wherein the fibrous layer is continuous.

10 9. A multi-layered moulding material according to any one of claims 1 to 8 wherein the fibrous layer is discontinuous.

15 10. A multi-layered moulding material according to any one of claims 1 to 9 wherein the resin system is a thermosetting polymer.

20 11. A multi-layered moulding material according to claim 10, wherein the thermosetting polymer is selected from epoxy, polyester, vinylester, polyimide, cyanate ester, phenolic and bismaleimide systems, modifications thereof and blends thereof.

25 12. A multi-layered moulding material according to any one of claims 1 to 11, wherein the or each fibrous layer is formed from glass fibres, carbon fibres, polyethylene fibres, aramid fibres, natural fibres or modified natural fibres.

30 13. A multi-layered moulding material according to any one of claims 1 to 12, wherein the fibres in the fibrous layer or layers are unidirectional.

35 14. A multi-layered moulding material according to any one of claims 1 to 13, wherein the resin layer is a conventional prepreg.

15. A multi-layered moulding material for use in the production of a surface layer comprising a multi-layered moulding material according to any one of claims 1 to 14.

5

16. A multi-layered moulding material according to any one of claims 1 to 15, wherein the fibrous layer comprises a surface material which gives a high quality surface substantially free of pinholes or surface porosity.

10

17. A multi-layered moulding material for use in the production of a surface layer according to claim 15 or 16 in which a woven fibrous layer is conjoined to one surface and a nonwoven fibrous layer is conjoined to the opposing 15 surface.

18. A method of forming a preform multi-layered material of any one of claims 1 to 17 by placing the or each fibrous layer in contact with the resin layer.

20

19. A method according to claim 18, wherein the resin is coated onto a support prior to being contacted by the fibrous layer.

25

20. An article of manufacture produced from the moulding material of any one of claims 1 to 17 or made in accordance with any one of claims 18 or 19.

30

21. A method of forming the article of manufacturing of claim 20 in which the moulding material is placed in contact with the mould and allowed to cure.



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(56) Documents Cited:	GB 1248060 A EP 0807514 A EP 0224064 A WO 1998/034979 A1 DE 003536272 A DE 003243925 A US 5639552 A US 5431995 A US 4311661 A US 3790432 A	

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Fig.1.

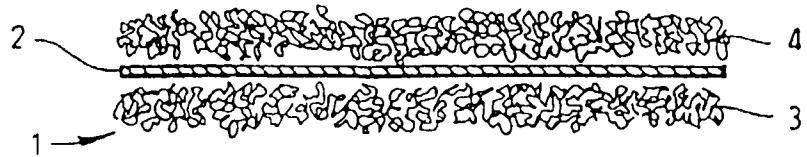


Fig.2.

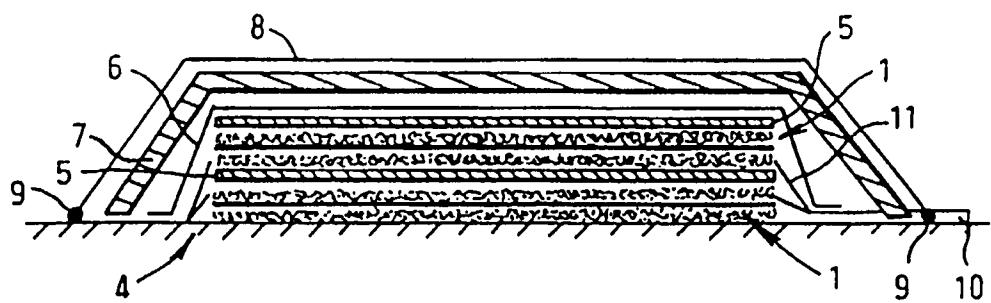
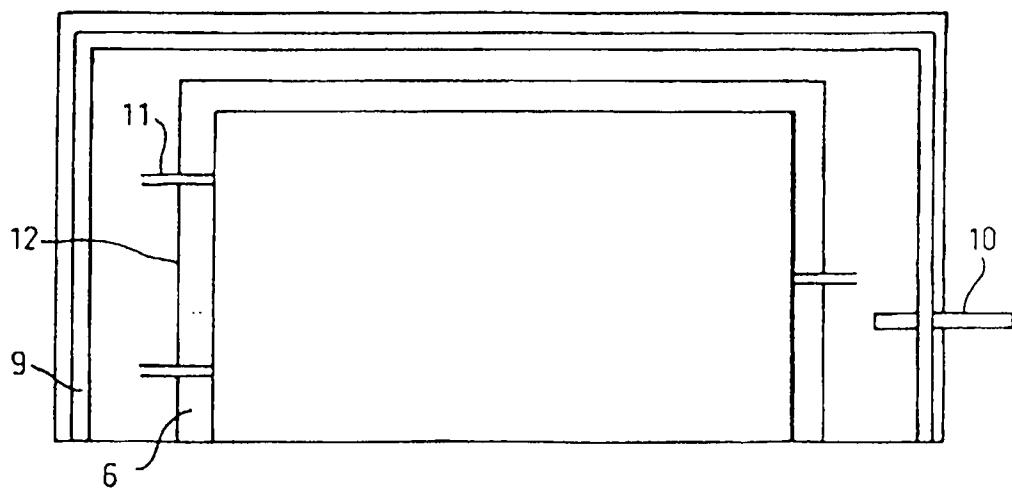


Fig.3.



MOULDING MATERIALS

The present invention relates to moulding materials. More particularly, it relates to composite moulding materials 5 which include fibres in their structure which in the moulded product will provide reinforcement.

Historically, mouldings were formed from resin either alone or reinforced with fibres. However, whilst in principle the 10 products were satisfactory, where fibres were present, it was difficult to control the ratio of the resin to the reinforcement fibres and thus the quality of the products produced was not consistent. The process was therefore refined such that the supplier of the resin provided the 15 producer of the moulded article with a pre-impregnated reinforcement known as a "prepreg". The moulder is then able to produce the moulded article from the pre-impregnated material confident that the ratio of resin to fibre is correct. Thus, the present invention is 20 particularly directed to preformed prepregs.

It will be understood that conventionally "prepregs" are fibrous composite materials which comprise fibres embedded in a matrix of resin and which are provided in the form of, 25 for example, sheets, strips, or continuous rolls, which can then be placed in contact with a mould prior to the resin being cured to form the moulded product. A prepreg may comprise unidirectional fibres or the fibres may be multi-directional. In use, several layers of prepreg may be 30 layered prior to curing to form a laminate product.

The most basic form of prepreg is prepreg tape or strip. These tapes or strips comprise unidirectional non-woven fibres held together by resin. These tapes are attractive 35 as the straight fibres provide the finished moulding with

good mechanical properties. Further the good packing of the fibres reduces the amount of resin required in the laminate. However, as these tapes have little porosity through their thickness, when multiple layers are used
5 together the tapes or strips trap substantial volumes of air which will lead to voids in the cured laminate. For the purposes of this application the term prepreg will be used to refer not only to composite materials where the fibres are embedded in the resin but also to those where
10 they are in contact with it.

Howsoever formed, when such prepgs are layered to produce a thick laminated product, certain drawbacks and disadvantages can arise. A thick laminated product is
15 generally understood to have a thickness greater than 2mm and is preferably greater than 4mm and may extend to 40mm.

A particular disadvantage of such thick products is that air can become trapped either within a layer of the
20 moulding material or between adjacent layers. The presence of intra-, inter- or intra- and inter-laminar air can lead to voids being formed in the finished cured product. Such voids can result in the laminate having reduced mechanical properties and can lead to premature failure of the
25 composite material.

Many techniques have been suggested to reduce the occurrence of such voids. One such technique is that of frequent vacuum debulking in which a few layers are laid in
30 the mould and consolidated using vacuum before further layers of moulding material are laid onto the laminate formed in the first step. However, whilst this technique may go some way to addressing the problem of void formation, a void content of 2 to 5% will still commonly be
35 present. Further, the technique of vacuum debulking, whilst

being somewhat effective, is labour intensive and is therefore costly and hence not desirable.

The problem of void formation is particularly exacerbated
5 when heavyweight material, for example 1200 g/m² glass
fibre unidirectional tape, is used in the production of the
moulding. It will be understood that it is desirable to use
heavyweight materials in moulding production since their
use makes it possible to produce the finished product from
10 fewer layers thereby reducing the costs both of labour and
materials. However, where heavyweight material of this kind
is used, void formation is particularly prevalent since
such materials are generally impervious to air movement
through their thickness.

15 It has been suggested that interleaving dry reinforcement
layers between the layers of the prepreg as the laminate is
built up can reduce the problem of void formation. However,
whilst this technique does go some way towards addressing
20 the problem of void formation, the presence of the dry
reinforcement layer reduces the relative resin content of
the finished product which may have a detrimental effect on
the strength of the finished product. Whilst it is possible
25 to compensate for the loss of resin from the prepreg to the
dry reinforcement layers by providing additional resin in
the prepreg, such increased resin content materials are
difficult to handle because of their high tack and low
drape. It is also important that there is complete
30 coincidence of the resin rich prepreg and dry layers
throughout the laminate or resin rich or resin lean areas
will result.

A similar assembly to the above described interleaved
laminate is disclosed in document US-A-4 311 661. This
35 document describes a process for producing a resin-fibre

composite article with a relatively low void content. The process comprises the step of forming an assembly on the surface of a mould, the assembly comprising individual layers consisting of a resin film, fibrous reinforcement 5 layers, a porous parting film and a bleeder layer which are each individually laid up. The process further comprises the step of applying a vacuum to the assembly and heating the assembly to cause the resin film to melt and impregnate upwards from the mould surface through the reinforcement 10 layer, the porous parting film and into the bleeder layer to completely saturate both the fibrous reinforcement layer and the bleeder layer. After the impregnation stage, the assembly is further heated at a sufficient temperature and pressure to effect final curing of the resin. After curing, 15 the composite article is retrieved by removing the bleeder layer and the parting film from the assembly.

A disadvantage of this particular process is that the resin layer, reinforcement layer and bleeder layer are each laid 20 up separately which is labourious. Also, the process is unnecessarily complicated because of the requirements of a bleeder layer and a parting film which need to be installed and later removed. To achieve a complete wetting out of both the reinforcement layer and the bleeder layer by 25 upward impregnation, the evacuation time and vacuum pressure depend on the thickness of the reinforcement layers in the assembly. For a large thickness of reinforcement material, the evacuation time can be substantial. Another problem associated with this material 30 is that it requires handling of a resin film. These films are either hard, brittle, inflexible materials which do not adapt to the shape of the mould when they are laid up, or these films are soft, tacky and sticky which prevents them from being easily handled and re-positioned in the mould. 35 The form of the film during handling depends on its

formulation and temperature. A further problem is that it is difficult to achieve an optimal ratio of the reinforcement material and the resin material. For a particular assembly, the required optimal amount of resin 5 must be found by trial and error. Another problem is that of tailoring of the assembly. In most composite structures the laminate is not uniform. The laminate is normally made thinner in areas of low loads or stresses and reinforced (thicker) in areas of high loads or stresses. This process 10 is called tailoring. In the process of document US-A-4 311 661, tailoring requires adaptation of both the resin film and the reinforcement layers which is labour intensive. If any tailoring has not been achieved correctly (the resin/reinforcement fibre ratio is not optimal in the 15 laminate locally) the structure of the moulded article is impaired.

Document DE-A-35 36 272 relates to a method of fabricating a composite part from a pre-shaped moulding material in a 20 mould. According to this method, the preshaped moulding material comprises a layer of a resin material and a layer of a fibrous material. The resin layer is formed in the shape of the mould (pre-shaped) before it is laid up. This is achieved by forming a support film (foil) in the shape of 25 the mould and spraying resin material onto the film. After the resin layer is shaped, dry fibrous material is provided on the resin layer. The pre-shaped moulding material is processed in the mould by applying both pressure (vacuum) and heat.

30

Similar to document US-A-4 311 661, the evacuation time depends on the thickness of the fibrous layers, and consequently, for thick layers of reinforcement material, the evacuation time can be substantial to achieve complete 35 impregnation of the fibrous layers. Other disadvantages of

this method are that during the composition of the moulding material outside the mould, a support film is necessary to support the material. Fabrication according to this method is therefore complicated and inefficient, since it requires 5 an additional pre-shaping step of the material before the material is laid up in the mould. Finally, for a particular composite part, the optimal reinforcement/resin ratio along every position of the mould surface must be established by trial and error, since the thickness of both the resin 10 layer and the reinforcement layer may vary depending on the shape of the mould.

Both of the afore described methods are impractical and difficult to use in a production environment, particularly 15 in a production environment in which complex moulds and moulds of varying shapes are used. The afore described methods are also complicated and require a lot of expertise and skill from the fabricator.

20 We have now found that the aforementioned problems can be solved by the provision of a multi-layered moulding material comprising a layer of resin material and conjoined to at least one surface thereof a fibrous layer.

25 Thus, according to a first aspect of the present invention, there is provided a preform multilayered moulding material according to any of the accompanying claims.

In an embodiment of the invention, the fibrous layer may be 30 held in place by the inherent tack of the surface of the resin layer. In a further embodiment, the fibrous layer may be partially impregnated by resin.

In an embodiment of the invention, the resin layer may 35 itself be a conventional prepreg.

In a particularly preferred embodiment, the multi-layered moulding material comprises three layers wherein a central resin layer has a fibrous layer conjoined to either side.

- 5 In one alternative arrangement, the multi-layered moulding material comprises five layers in which the two outer layers are dry fibrous layers each attached on its inner surface to a resin film layer. The resin film layers are themselves adhered to a further dry fibrous layer which
- 10 forms the central (fifth) layer. The resin layers in this multilayered material may be formed from different resins.

Larger multi-layered structures may also be formed in which dry fibrous layers are attached to a resin film layer.

- 15 Again, the resin film layers in this multi-layered material may be formed from different resins.

The resin layer may be a conventional prepreg.

- 20 Thus, in one particularly preferred embodiment, the outer surface of the moulding material is free from resin and is therefore dry to the touch due to the presence of the two fibrous layers and can therefore be handled readily.

- 25 In one alternative arrangement, the multi-layered moulding material may have a tackifier or a binder material applied to at least one surface.

- 30 Without wishing to be bound by any theory, it is believed that when the material of the present invention is used alone, laminated with further layers of moulding material of the present invention or laminated with layers of conventional prepreg, the fibrous layer of the material of the present invention performs in a similar manner to the dry layers of reinforcement of the conventional systems, in
- 35

that it allows entrapped air to pass out of the laminate.

The void content for a product produced from, or including,
the moulding material of the present invention will
5 generally be less than 2% and is commonly less than 0.5%.

One particular benefit of the arrangement of the present
invention is that the amount of resin present in the multi-
layered moulding material can be controlled such that when
10 the material is cured, the correct amount of resin will
flow into the dry fibrous layers and there will be no
reduction in the cured resin content.

The moulding material of the present invention surprisingly
15 offers a number of advantages over the conventional
moulding materials. One particular benefit of the present
invention is that the moulding material exhibits improved
handling characteristics when compared to those of
conventional materials in that it is more flexible, that is
20 to say it has improved drape and can therefore be used in
the production of more complex mouldings. It has been found
that the moulding material of the present invention having
a fibre weight of 3,500 g/m² has better drape than a
25 comparable conventional prepreg having a fibre weight of
1,700 g/m².

Further, it has been found that the moulding material of
the present invention exhibits significantly lower tendency
to bridge across details in a moulding. Without wishing to
30 be bound by any theory, we believe that this is due to the
abilities of the plies to slide over each other during the
consolidation and curing stages. Further, even if bridging
does occur, the moulding material of the present invention
tends to fill any bridged areas with resin rather than
35 leave a void in the laminate. Again, without wishing to be

bound by any theory, we believe that this is due to the fact that the potential void has been evacuated by the excellent air transport properties of the material of the invention and thus resin can fill the potential void as no 5 air is trapped. By this means a high quality finished product may be obtained. This is in contrast to conventional materials, where imperfections may be noted in the surface of the moulding at complex mould areas, such as corners due to bridging of mould areas by the moulding 10 material. It is therefore possible to use the moulding material of the present invention in the production of more complex shapes than has been achievable heretofore.

In conventional prepgs that are processed under vacuum 15 consolidation, it is important that dry areas of reinforcement fibres are avoided since they generally do not completely wet out during the production of the prepg which may lead to areas of weakness in the finished product. However, where the moulding materials of the 20 present invention are used, the fibrous layer is specifically not wet out during production of the prepg but will be completely wet out during the processing.

As the improved moulding material of the present invention 25 exhibits these improved characteristics, it is possible to use heavier weight prepgs than has been possible using conventional prepg technology. With conventional technology, even when heavy weights are produced, they are difficult to handle and therefore are not desirable. 30 However, since the moulding materials of the present invention exhibit improved drape characteristics, even heavier weight prepgs may be handled readily.

Any suitable thermoset resin may be used in the production 35 of the moulding material of the present invention.

Particularly suitable resin systems include the epoxy, polyester, vinylester, polyimide, cyanate ester, phenolic and bismaleimide systems. Suitable epoxy resins include diglycidyl ethers of bisphenol A, diglycidyl ethers of bisphenol F, epoxy novolac resins and N-glycidyl ethers, glycidyl esters, aliphatic and cycloaliphatic glycidyl ethers, glycidyl ethers of aminophenols, glycidyl ethers of any substituted phenols, monomers containing methacrylate groups (such as glycidyl methacrylates, epoxy acrylates and hydroxyacrylates) and blends thereof. Also included are modified blends of the aforementioned thermosetting polymers. These polymers are typically modified by rubber or thermoplastic addition.

Any suitable catalyst may be used. The catalyst will be selected to correspond to the resin used. One suitable catalyst for use with an epoxy resin is a dicyandiamide curing agent. The catalyst may be accelerated. Where a dicyandiamide catalyst is used, a substituted urea may be used as an accelerator. Suitable accelerators include Diuron, Monuron, Fenuron, Chlortoluron, bis-urea of toluenediisocyanate and other substituted homologues. The epoxy curing agent may be selected from Dapsone (DDS), Diamino-diphenyl methane (DDM), BF3-amine complex, substituted imidazoles, accelerated anhydrides, metaphenylene diamine, diamino diphenylether, aromatic polyetheramines, aliphatic amine adducts, aliphatic amine salts, aromatic amine adducts and aromatic amine salts. Also suitable for systems containing acrylate functionality are UV photoinitiators such as those which liberate a Lewis or Bronstead acid upon irradiation. Examples include triarylsulphonium salts which possess anions such as tetrafluoroborate or hexafluoroborate.

The resin system may also include additives relevant to the

production of the moulding such as hardeners. Other additives may be included to effect the finished moulding such as pigments, UV stabilising additives, anti-mould, anti-fungal and flame retardant additives. Whatever 5 additives are added, it is important to ensure that the viscosity of the resin is sufficiently low during the curing and consolidation steps. If it is not, it will not wet out the dry layers.

10 The fibre layer or layers may be formed from any suitable fibres. Suitable fibres include glass fibres, carbon fibres and polymeric fibres such as polyethylene fibres and aramid fibres. Suitable glass fibres include those made from E-glass, S-glass, C-glass, T-glass or R-glass. Suitable 15 aramid fibres include those sold under the trade marks KEVLAR and TWARON HM. Ballistic grade aramid fibres may be utilised where this characteristic is required due to the intended use of the finished product. Organic fibres and modified organic fibres such as jute or hemp may also be 20 used.

The fibrous layer may comprise fibres of only one kind or different types of fibre may be combined in the fibrous layer.

25 The fibres may be used alone or in combination. The fibres may be used in the form of tissue, chopped strand mat, continuous mat, woven fabrics, stitched fabrics, or simple rovings. Any suitable fibre size may be used. Particularly 30 preferred are E-glass yarns having a filament diameter of 5 to $13\mu\text{m}$ and 11 to 136 tex or E-glass rovings having a filament diameter of 10 to $16\mu\text{m}$ and 600 to 2400 tex. The fibrous material may be preformed before being laid on to the resin layer or alternatively, loose fibres may simply 35 be laid onto the resin layer.

In a particularly preferred arrangement, the fibres are arranged such that they are unidirectional. Where the moulding material of the present invention comprises two fibrous layers conjoined to opposing faces of the resin 5 layer, the fibrous layers may be orientated in the same direction or in different directions. In particular, the fibre orientation of the skins of the sandwich material may be 0°, 90°, 0°/90°, +/-45° or quasi isotropic or 0°/+45°/-45°.

10

In an embodiment of the invention the adhesive properties of the resin layer may be sufficient to retain the fibrous layer howsoever formed in position. In another embodiment the fibrous layer may be retained against the resin layer 15 by means of an adhesive. It will be understood that the adhesive will not prevent the travel of the resin into the fibrous layer during production of the product.

In one alternative embodiment, a tackifier and/or a binder 20 material may be applied to one or both surfaces of the multi-layered moulding material. The tackifier/binder is preferably applied as a light covering. Typically, the tackifier/binder may be applied in an amount of 0.5% to 7% of the fibre weight.

25

The presence of the tackifier/binder serves a number of functions. First, it may provide a degree of tack to the surfaces of the material therefore assisting adjacent layers of material to be held together during processing.

30

Secondly, the presence of the tackifier/binder serves to stabilise the fibrous layers and thereby improves the integrity of the surface of the prepreg. This is particularly important where the fibrous layers on the 35 faces of the improved prepreg are made from pure rovings or

tows of fibres rather than of woven or stitched materials. The material of this embodiment may have improved handling characteristics and may be less likely to be damaged by handling prior to moulding.

5

Where a tackifier/binder is present, it may also serve as an interply toughening agent which can give significant improvements in interply fracture energy.

10 Any suitable material may be used as a binder/ tackifier. Particularly suitable materials include high molecular weight resins. These resins may be used alone or in combination with additives including toughening agents and curing agents.

15

The tackifier/binder may be applied to the material by any suitable means including spraying using carrier solvent, hot melt techniques or dry powder applications. In a particularly preferred arrangement, the tackifier/binder 20 forms discrete particles on the surface of the fibres rather than a uniform coating. The tackifier/binder may be applied to the material at any suitable time during its manufacture.

25 The arrangement of the structure of the fibres in the fibrous layer or of the fibrous layer itself may be altered depending on the properties required to be exhibited in the finished end product. For example, where the product is to be a high performance composite mould tool, it is 30 preferable to use discrete areas of reinforcement rather than continuous lengths. Conventionally, these small areas are of the approximate size 300mm x 300mm. Although the use of fibrous materials having discrete areas of reinforcement offer a range of benefits, they have not generally been 35 accepted by some fabricators in the past as their use is

labour intensive. This is particularly the case where the moulding is large in size and comprises several layers. In this connection, it is noted that in the fabrication of, for example, composite tools, the moulding may be made of 5 about 20 layers and be 20 to 50 m² in area.

It will be understood that a moulding material in accordance with the present invention may be readily formed by laying pieces of fibrous material, of the desired size 10 onto the resin layer. Thus according to a further preferred aspect of the present invention there is provided a moulding material in which the or each fibrous layer comprises discrete pieces of fibrous material. Thus the fibrous layer may be discontinuous.

15 The benefit associated with materials formed in this way is that the fabricator can simply roll out the material and the need to separately attach, for example, squares of fibrous material is obviated. As with conventional 20 materials, the materials with these discrete areas of fibres nest down to conform to the tool profile and the risk of bridging areas of the mould leading to the formation of voids is further minimised. The reduced fibre length present in a material of this type also reduces 25 stresses which may arise in the finished laminate. These stresses result from thermal or cure shrinkage and may result in delamination or even change of shape of the tool.

30 The discrete panels of fibrous material used to form the fibrous layer of the moulding material of the present invention are preferably squares 300mm x 300mm. Where the moulding material comprises two fibrous layers located on opposing faces of the resin layer, the discrete panels are 35 preferably arranged such that the joints between panels on the upper layer are staggered from those between panels in

the lower layer. Thus the inherent strength of the material is not compromised.

5 The moulding materials of the present invention may be formed readily by contacting the resin layer with the or each fibrous layer.

10 Thus, according to a second aspect of the present invention there is provided a method of forming a moulding material in accordance with the above first aspect of the invention in which a fibrous layer is placed in contact with a resin layer.

15 The moulding material of the present invention may be made by any suitable method. However, hot-melt techniques are particularly preferred.

20 In one method, the resin mixed with catalyst and any additives is preferably coated onto a support, such as siliconised paper substrate prior to being contacted by the fibrous layer. The resin is preferably coated onto the substrate using a conventional filmer. The coating is preferably laid onto the substrate at a raised temperature. The temperature selected will depend on the resin used, 25 however a suitable temperature will be in the region of 60°C.

30 The weight of the resin coated on the support will depend on the properties required of the finished prepreg. However, the weight is generally from 20 to 1,200 g/m² .

The coated substrate may be passed over a chill plate at about 5°C to reduce the temperature of the resin.

35 Where it is desirable to form a moulding material having

fibrous layers located on both sides of the resin layer several methods are available. In one method, two prepgs are formed as described above, the substrates are removed and the two prepgs are then combined with the two 5 resinous sides being placed together such that the fibrous sides are located apart from each other such that they are on the outer faces of the resulting sandwich. When the two resin layers unify the resulting moulding material has a central resin layer conjoined on each face to a fibrous 10 layer.

In one alternative arrangement, a moulding material comprising a resin layer and a single fibrous layer produced as described above is turned such that it lies on 15 the dry fibrous layer, the support is removed and a fibrous layer may then be placed on the exposed resin surface.

In another method a carrier fabric or tissue is coated on both sides with a resin film and the dry fibrous layers are 20 combined onto each face of the resin film.

In a further alternative method, a fibrous layer is laid as a support and the resin layer is then coated thereon. The second fibrous layer may then be readily laid onto the 25 exposed surface.

The process may be mechanised and may be a batch process or a continuous process.

30 Once the moulding material of the present invention is formed it may be rolled. An interleave material may be used. A particularly suitable interleave material is a polyethylene interleave.

35 The moulding material of the present invention may be

readily stored until required. The shelf life will be dependant on the resin system. It is preferable that the material is stored at temperatures below zero (most preferably -18°C to -4°C). At ambient temperature, the

5 product has a shelf life in the region of 5 to 55 days, dependant on resin system and fibre weight. After the expiry of the shelf life period, the product is still usable but will have the characteristics and properties of conventional prepgs.

10

Moulding materials of the present invention or made in accordance with the second aspect of the present invention may be used alone, laminated with further layers of moulding material of the present invention or laminated 15 with conventional prepg materials. The materials may be processed by any suitable method and are preferably cured by means of a vacuum processing technique to form high quality laminates.

20

A further advantage of the moulding material of the present invention is that the thick section, i.e. one having thickness greater than 4mm, preferably about 10mm, may be produced in a single operation with no requirement for intermediate consolidation debulking stages.

25

Where a vertical mould surface is to be coated, a combination of the moulding material of the present invention is preferably used in combination with conventional prepgs as the high tack of the conventional 30 material will help to hold the material of the present invention in place. Alternatively, a moulding material of the present invention coated with tackifier/binder may be used.

35 The moulding material of the present invention is

particularly suitable for use in combination with prepreg tape. The combination of the moulding material of the present invention and the prepreg tape is particularly advantageous since the material of the present invention 5 allows the tape to breathe such that void formation is reduced or even obviated. Further, the arrangement allows even poor quality tapes having dry or partially wet out fibres to be used since on curing the fibres will wet out completely such that a high quality laminate is formed.

10

In use, once the layers of the laminate have been laid into the mould, the resin is cured. It is desirable that a cure schedule is selected whereby the temperature is held at a point where the resin viscosity is low. The cure schedule 15 selected will depend on the resin used.

Particularly improved results in processing the material of the present invention may be obtained where care is taken to ensure that the dry fibrous layers are in contact with a vacuum system to ensure that entrained air can be fully 20 evacuated. One method of achieving the contact between the dry fibrous layers and the vacuum system is to cut the moulding material of the present invention larger than is conventional and then linking it to the vacuum system via an air breathable media. Suitable media include a non-woven 25 breather, woven breather or dry fibrous strands or tows. Suitable non-woven breathers include nylon felted material of 150 g/m².

Where required a coating may be applied to the moulding. 30 The coating may comprise a conventional gel coat system. Suitable gel coat systems include epoxy with the incorporation of a variety of fillers and pigments. Polyester or vinylester gelcoats may also be used.

35 Whilst these gel coats, provide satisfactory results, they

are labour intensive to use. We have now found that an improved coating may be obtained by the use of a modified moulding material of the present invention which is used as the layer closest to the mould. The modified moulding 5 material comprises a layer of resin having a lightweight woven cloth on one face and a non-woven tissue on the other face. This material applied to a tool with the woven cloth facing the mould and backed up with either a conventional moulding material or a moulding material in accordance with 10 the present invention gives a high quality surface substantially free of pinholes or surface porosity.

Thus according to a further aspect of the present invention there is provided a moulding material for use in the 15 production of a surface layer comprising a resin layer having a fibrous layer conjoined to each surface thereof. The material conjoined to one surface is preferably a woven material and the layer conjoined to the opposing surface is preferably nonwoven. The fibrous layers are preferably 20 produced from glass fibres. A light weight fibrous layer, typically 20gm/m².

The woven surface layer generally wets out during the consolidation process. Any suitable woven cloth may be 25 used. However, in a particularly preferred arrangement the material is selected to have a good light stability and to improve the appearance of the finished product.

The moulding materials of the present invention may be used 30 in the production of a wide range of products. Examples include products used in the marine industry such as boat hulls, masts, spars; the aerospace industry such as fuselage parts; the motor industry such as car, van or lorry body parts; the sports industry such as surf boards, 35 sailboards, and other sports equipment such as bicycles or

hockey sticks, and those used in other industries such as composite tools, composite tubes and turbine blades such as those used in wind turbines.

5 Thus, according to a further aspect of the present invention there is provided an article of manufacture produced from the moulding material of the first aspect of the present invention or made in accordance with the second aspect of the present invention. There is also provided a
10 method of forming the article of manufacture in which the moulding material is placed in contact with a mould and then allowed to cure.

15 The moulding material of the present invention may be used alone or laminated with one or more layers of moulding material in accordance with the present invention or conventional moulding materials.

20 The invention will now be described by way of example with reference to the accompanying example drawings in which:

25 Figure 1 is schematic diagram of a three layered moulding material in accordance with the present invention;

Figure 2 is schematic diagram of the apparatus used in the production of the moulding material of the present invention; and

30 Figure 3 is schematic diagram of an alternative apparatus.

35 As illustrated in Figure 1, the moulding material of the present invention 1, comprises a central resin film 2 having fibrous layers 3 and 4 located on opposing faces

thereof.

In use, this material 1 is laid on the tool surface 4. The material may be laminated with other materials of the 5 present invention or with conventional prepgs. In the arrangement illustrated in Figure 2, two layers of moulding material in accordance with the present invention is interleaved with layers of conventional prepg 5. This stack is preferably surrounded by a non-perforated film 6, 10 a breather 7 and a vacuum film 8. The vacuum film 8 is sealed to the tooling by means of sealant tape and the air is evacuated during the curing process via vacuum line 10.

Curing is preferably effected at temperatures above 15 ambient.

Glass rovings 11 may be utilised to assist the perimeter air bleed. These glass rovings are particularly advantageous where a zero bleed mode of processing is used. 20 The glass rovings are put through the non-perforated film to assist in the evacuation of air from the laminate stack. To further assist the removal of air, glass rovings may be placed through the non-perforated film in the centre of the panel. These allow air to bleed from the centre of the 25 panel and also connects the moulding materials of the present invention in the laminate together in the z-axis thereby further assisting evacuation of air.

When making sandwich laminates in one operation it is 30 beneficial to have air bleed holes in the core. These allow the air to escape from the underlying laminate thus preventing any closing off of the material under the foam block. Saw cuts in the lower face of the core around the perimeter may also be used to eliminate any closing off 35 effects of the core edge. The saw cuts are typically 2mm

deep by 1 mm wide and end 8cm long at a spacing of every 8cm.

5 The apparatus illustrated in Figure 3 is very similar to that of Figure 2 but is appropriate for use with a large laminate stack.

10 A suitable cure schedule involves holding the temperature at a point where the resin viscosity is low, for example, 10 poise to 100 poise for a period of 4 hours, and remains low for sufficient time for the resin to wet out the fibres of the fibrous layer or layers. A typical cure schedule would be to ramp from 25 to 70°C, a dwell at 70°C for four hours, ramp to 85°C and then held at 85°C for 10 hours. On 15 this schedule a typical resin viscosity would drop down to 40 poise and at the end of the four hour dwell has only risen to 100 poise. The ramp rates to 70°C or 85°C are not critical. However, they will normally be in the range of 0.1 to 10°C/min.

20

Example 1

25 A prepreg according to the present invention was formed by laying unidirectional E-glass woven reinforcement of 500 g/m² on opposing sides of a layer of 430 g/m² resin. This prepreg was interleaved with layers of conventional prepreg tape of 1200 E-glass with a resin content of 30% by weight. In both types of prepreg the resin used was the SP Systems 30 SE90 available from SP Systems of Structural Polymer (Holdings) Limited of Isle of Wight. The resin is a high flow, 85 to 120°C cure, non-toughened epoxy prepreg cured by an accelerated dicyandiamide curing agent. SE90 prepreg is an epoxy prepreg.

35 The laminate stack was then covered with nylon peel ply and

a microperforated release film, a layer of 150g non-woven breather material and an impervious nylon vacuum bag.

5 A vacuum of 90% was applied and the assembly heated from ambient to 70°C at 0.3°C/min. The temperature was then held at 70°C for 4 hours. The temperature was then ramped up to 120°C and then held for one hour. The laminate was then cooled to ambient temperature and the laminate was demoulded and examined.

10

On examination it was noted that the dry reinforcement layers had completely wet out and the laminate was free of entrapped air.

15 The void content of the laminate was determined by measuring the specific gravity of the sample by weighing it in air and water. The laminate was then put in an oven at 650°C to burn off the resin. From the weight loss and the densities of the resin and the glass, the void content was 20 calculated. Measurements showed the void content to be less than 0.25%. The final fibre volume fraction was 56%.

Whilst the moulding material of the present invention has been described as having at two or three layers, it will be 25 understood that a multi-layer moulding material in accordance with the present invention, may be supplied to the fabricator in an arrangement which comprises more than three layers due to the combination of several layers of the moulding material of the present invention together.

30

CLAIMS

1. A preform multi-layered moulding material adapted for use in multiple layers, said multi-layered
5 moulding material comprising a layer of resin material and having conjoined to at least one surface thereof a fibrous layer by contacting the respective layers without any substantial impregnation, said fibrous layer of said moulding material being held to said resin layer by
10 inherent tack of the adjacent surface of the resin layer such that said fibrous layer is at least partially unimpregnated with said resin to allow entrapped air to pass out of said multi-layered moulding material during processing of the material.

15

2. A multi-layered moulding material according to claim 1 wherein a first fibrous layer is conjoined to the upper surface of the resin layer and a second fibrous layer is conjoined to the lower surface of the resin layer.

20

3. A multi-layered moulding material according to claim 2, wherein the outer surface of the moulding material is free from resin and is dry to touch.

25

4. A multi-layered moulding material according to claim 2 or 3 wherein the first and second fibrous layers are formed from the same material.

30

5. A multi-layered moulding material according to claim 2 or 3 wherein the first and second fibrous layers are formed from different materials.

35

6. A multi-layered moulding material according to any one of claims 1 to 5 wherein the or each fibrous layer before contacting is partially impregnated by resin.

7. A multi-layer moulding material according to any

one of claims 1 to 6 wherein a tackifier and/or a binder is applied to one or both outer surfaces of the at least one fibrous layer.

5 8. A multi-layer moulding material according to any one of claims 1 to 7 wherein the fibrous layer is continuous.

10 9. A multi-layered moulding material according to any one of claims 1 to 8 wherein the fibrous layer is discontinuous.

15 10. A multi-layered moulding material according to any one of claims 1 to 9 wherein the resin system is a thermosetting polymer.

20 11. A multi-layered moulding material according to claim 10, wherein the thermosetting polymer is selected from epoxy, polyester, vinylester, polyimide, cyanate ester, phenolic and bismaleimide systems, modifications thereof and blends thereof.

25 12. A multi-layered moulding material according to any one of claims 1 to 11, wherein the or each fibrous layer is formed from glass fibres, carbon fibres, polyethylene fibres, aramid fibres, natural fibres or modified natural fibres.

30 13. A multi-layered moulding material according to any one of claims 1 to 12, wherein the fibres in the fibrous layer or layers are unidirectional.

35 14. A multi-layered moulding material according to any one of claims 1 to 13, wherein the resin layer is a conventional prepreg.

15. A multi-layered moulding material for use in the production of a surface layer comprising a multi-layered moulding material according to any one of claims 1 to 14.

5

16. A multi-layered moulding material according to any one of claims 1 to 15, wherein the fibrous layer comprises a surface material which gives a high quality surface substantially free of pinholes or surface porosity.

10

17. A multi-layered moulding material for use in the production of a surface layer according to claim 15 or 16 in which a woven fibrous layer is conjoined to one surface and a nonwoven fibrous layer is conjoined to the opposing 15 surface.

18. A method of forming a preform multi-layered material of any one of claims 1 to 17 by placing the or each fibrous layer in contact with the resin layer.

20

19. A method according to claim 18, wherein the resin is coated onto a support prior to being contacted by the fibrous layer.

25

20. An article of manufacture produced from the moulding material of any one of claims 1 to 17 or made in accordance with any one of claims 18 or 19.

30

21. A method of forming the article of manufacturing of claim 20 in which the moulding material is placed in contact with the mould and allowed to cure.